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The Thermal Decomposition of Irradiated Nickel Oxalate¹

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The thermal decomposition of unirradiated and reactor-irradiated dehydrated nickel oxalate has been studied in the temperature range 253–360°. Reaction begins at surface nuclei and there is evidence that the activation energy for nucleus formation is less than for the growth process. In those temperature regions where the amount of decomposition due to the growth of existing nuclei overshadows that due to growth of newly formed nuclei, the acceleratory region is described by a t^2 law. The value of the fraction of total decomposition (α) at the point where the rate is a maximum (the point of inflection) changes drastically with temperature and irradiation. Irradiation appears to increase the number of potential nuclei but does not enhance the growth rate.

Several recent studies^{4–6} of the thermal decomposition of nickel oxalate have been published. Attention has also been given to the compound silver oxalate^{7,8} which behaves similarly to the nickel salt. In both cases the curve representing α , the fraction of the total decomposition, *vs.* time is sigmoidal. Apparently conflicting rate laws for the acceleratory region have been reported which may be described as the “exponential” and “power” laws, given, respectively, by the equations

$$\alpha = Ae^{kt} \quad (1)$$

$$\alpha = Bt^m \quad (2)$$

The “exponential” form is generally regarded as indicative of a chain reaction whereby a growing nucleus can branch. The power law is interpreted in terms of a fixed topochemical decomposition scheme in which the power “ m ” depends upon whether the nuclei grow in one, two, or three dimensions and also depends on the law governing their rate of increase. The contradictions in the silver oxalate work have reportedly been resolved.⁸ There seems to be general agreement that aging of a crystal can influence the observed kinetic scheme.

The objectives of thermal decomposition studies are twofold, *i.e.*, answers must be found to the questions

where and how do reactions occur? The first question refers to the topochemical behavior while the second refers to the fundamental molecular step leading to the decomposition. Studies of the kind reported here throw light mainly on the first question and it is the object of the current investigation to find such answers with the use of irradiation which has proved to be a powerful tool in such probes.

Experimental

The nickel oxalate was prepared from the nitrate by slow precipitation at 70° in an ammonium acetate-acetic acid buffered solution with the oxalate ion

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(5) J. A. Allen and D. E. Scaife, *J. Phys. Chem.*, **58**, 677 (1954).

(6) V. Danes and V. Ponc, *Collection Czech. Chem. Commun.*, **23**, 858 (1958).

(7) A. Finch, P. W. M. Jacobs, and F. C. Tompkins, *J. Chem. Soc.*, 2053 (1954).

(8) R. M. Haynes and D. A. Young, *Discussions Faraday Soc.*, **31**, 229 (1961).

being furnished by hydrolysis of diethyl oxalate. This method, adapted from standard procedures, was used in an effort to minimize the precipitation of crystals of colloidal dimensions. The filtered precipitate was washed and dried at room temperature and then dehydrated at 200° in a muffle furnace. The particle size distribution is not known but the crystals are larger than colloidal size.

The decomposition yields only nickel and CO₂ and, within experimental error, eventually goes to completion. The course of the reaction was followed by measurement of the pressure of the CO₂ evolved in a closed system. A Pirani gage was used whose signal was reproduced on a Brown recorder so that data were obtained automatically. The reaction vessel was a long horizontal quartz tube heated by a furnace electronically controlled to $\pm 0.1^\circ$. At the part of the tube located at the center of the furnace there was a flat depression 2.5 cm. in length. Reaction occurred in this depression. Located in front of the main furnace and concentric with the tube was an auxiliary heater which could be maintained at 200°.

About 5 mg. of the material were weighed and placed in a small platinum bucket which was attached by a long stiff wire to an iron slug. This unit was placed in the quartz tube the end of which was then closed. After evacuation to about 10^{-5} mm., the platinum bucket was moved by magnetically acting on the slug so that the sample was located in that part of the quartz tube which was maintained at 200°. To remove surface moisture it was left in this position for about 2 hr. During this time the system was still open to the vacuum pump and a liquid nitrogen trap. The pump and trap were then closed off and the sample moved further along the tube into the part heated by the furnace. The crystals were then tipped out of the bucket into the depression and the bucket withdrawn. Pressures were immediately and automatically recorded. One advantage of this system is that final dehydration took place *in situ* and the samples were thereafter never exposed to the atmosphere. The reaction always occurred on a surface of nickel oxide; the latter was formed by oxidation of deposited nickel by air introduced between runs. The reaction rates thus found were the same within experimental error as those obtained with a bare quartz surface. Before decomposition the dehydrated crystals were a bright yellow.

It was decided that, in the time available for this study, the most profitable experiments would be a set of runs at different temperatures using unirradiated material and a similar set for material subjected to a particular dose of irradiation. A few preliminary neutron and γ -ray irradiations at different doses were

performed in order to determine the order of magnitude of the dose which would be effective in producing large observable effects. The irradiation chosen was reactor irradiation in the Brookhaven graph search reactor for 390 hr. at a flux of $10^{13}/\text{cm}^2$ (of which approximately 4×10^{11} were epi-Cd) at an ambient temperature of 70°. When the irradiated samples were transferred, they were in contact with an atmosphere. They too were subjected to the primary *in situ* heating procedure at 200° to ensure complete dehydration.

The irradiated material was found to be about 50% decomposed by the irradiation (prior to the thermal decomposition). This figure was obtained by evaluation of the average P_∞/w ratio where P_∞ is the pressure developed and w is the sample mass. At the end of all runs the temperature was deliberately raised to about 400° to ensure an accurate P_∞ value. Irradiated crystals were black.

Results

The Form of the α -t Curves. The decomposition was studied in the temperature range 253–360° which represents a much wider range than had been used in previous studies. A typical plot of α , the fractional decomposition, vs. time is shown in Figure 1. The open circles being experimental points for unirradiated material. The general form is sigmoidal with a gradual approach to the acceleratory region. There is a small initial gas evolution of one type observed by Jacobs and Kureishy,⁴ but the kinetics are obscured by the generally increasing rate before the acceleratory region proper. However, prior to the

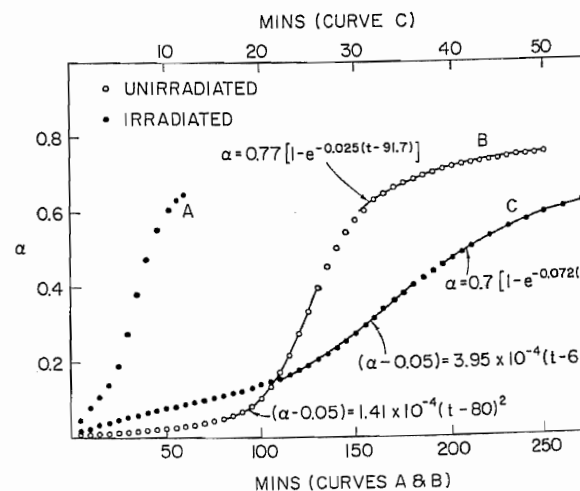
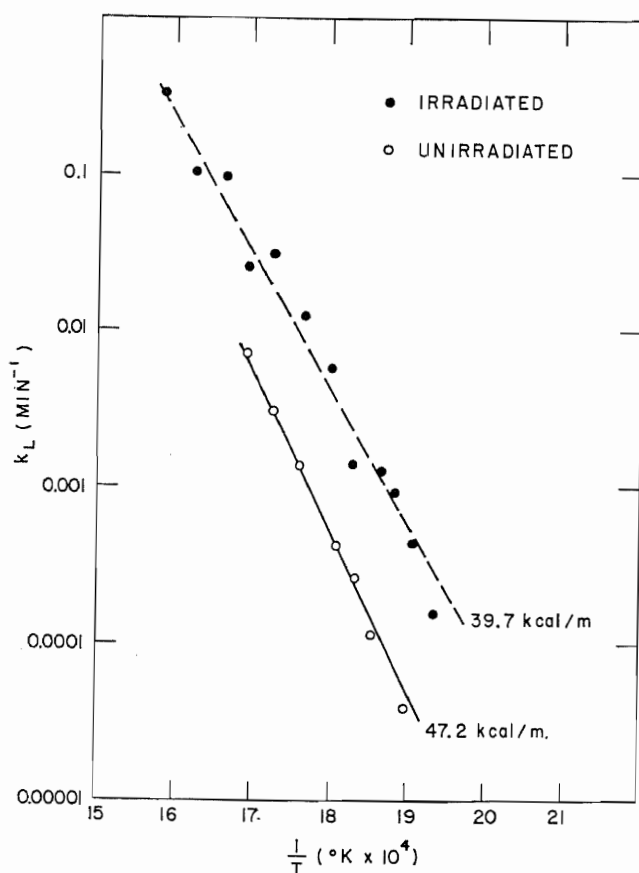


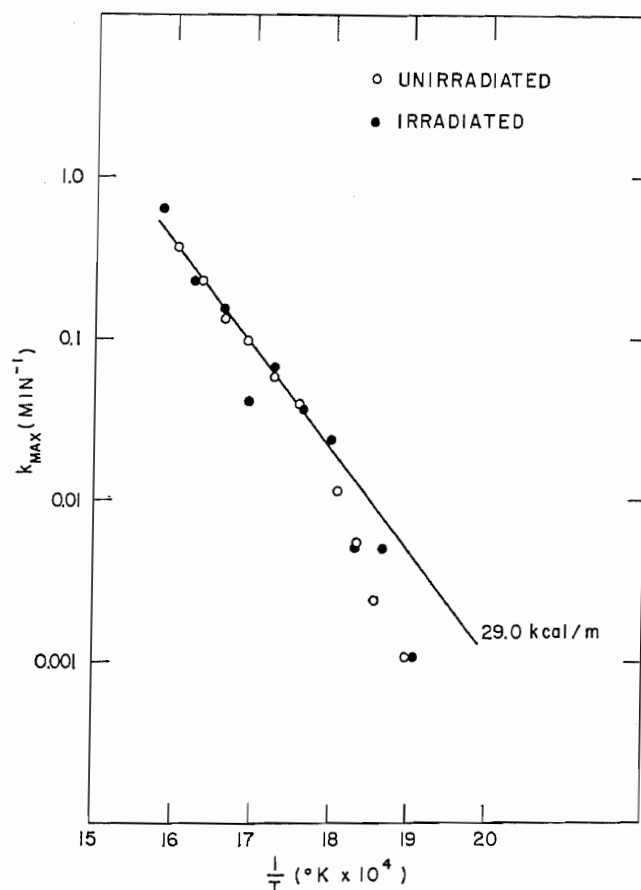
Figure 1. Fractional decomposition (α) vs. time: O, run for unirradiated material at 279.9°; ●, run for irradiated material at 282.7°.

Figure 2. Arrhenius plot of k_L .

celeratory region proper, it is possible to discern a linear region of low rate from which some kinetic information is obtainable. This rate, k_L , is simply the slope of the line in this region. The acceleratory region is followed by a maximum rate and a subsequent decay stage. The most satisfactory equation describing the acceleratory region is

$$(\alpha - \alpha_0) = a(t - t_0)^m \quad (3)$$

where a is a rate constant and t_0 and α_0 are constants which separate complicated initial reactions (such as initial surface reactions, etc.) from the acceleratory region.⁹ This technique has been extensively used in the field and provided due care is taken in curve analysis and interpretation very much useful information can be obtained from the power " m ". In the present case " m " was found to decrease somewhat with increasing values of α_0 but in general was close to a value of 2. It was found that increasing temperature brought " m " to a value of 2 with practically no α_0 correction. The same effect occurred with irradiation at all temperatures.

Figure 3. Arrhenius plot of k_{\max} .

The decay stage is best described by a simple exponential decay of the form

$$\alpha = D\{1 - \exp[k_d(t - t_0')]\} \quad (4)$$

Irradiation Effects. The effect of irradiation at a comparable temperature on the form of the α - t curve is shown alongside the "unirradiated" case in Fig. 1. Curve A has the same time scale as the "unirradiated" curve and shows the over-all shape. Curve C is the same run as A but with an expanded time scale to display more details about the acceleratory and decay stages. Three important effects are at once evident: (a) the time required to reach the maximum rate is drastically reduced by irradiation, (b) the value of the maximum rate itself is *not* affected (see also Fig. 3), and (c) the value of α at the point of inflection, *i.e.*, α_{\max} , is reduced.

Temperature Effects. Arrhenius plots are shown for the following parameters: (1) the quantity k_L in Fig. 2; (2) the maximum rate, k_{\max} , in Fig. 3 (this is

(9) Once α_0 has been chosen, t_0 follows since the point α_0 , t_0 corresponds to an actual point on the experimental curve.

merely the slope of the curve at the point of inflection); (3) the quantity k_d in Fig. 4.

A few general features of these plots are worth noting. First, irradiation has no effect on rate or activation energy for the region beyond the acceleratory stage, while it decreases the activation energy and increases the rate in the early stages of the reaction. Second, there is a complex temperature dependence of the maximum rate in the sense that a simple classical

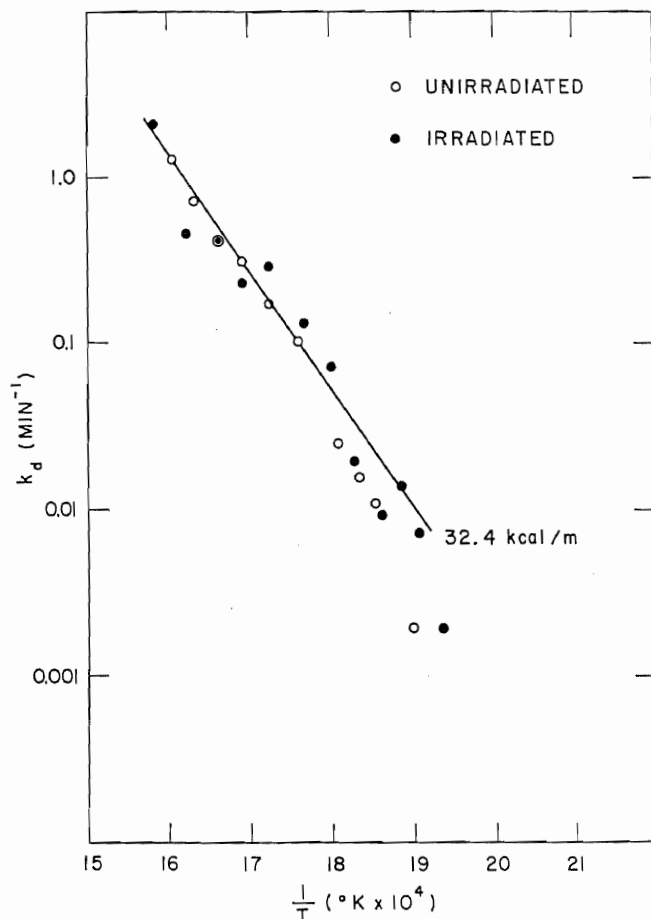


Figure 4. Arrhenius plot of k_d in the equation $\alpha = D[1 - \exp\{-k_d(t - t_0)\}]$.

straight line Arrhenius plot is not observed. This complexity is much smaller for the k_d plot, *i.e.*, for the end of the reaction.

Another temperature effect is that of the quantity α_{\max} which is the value of α at the inflection point or maximum rate. A plot of this *vs.* temperature is shown in Fig. 5. With unirradiated material a large increase of α_{\max} with temperature is evident (from 32% to about 48%). Irradiation results in a marked decrease of α_{\max} and although it is possible that here too

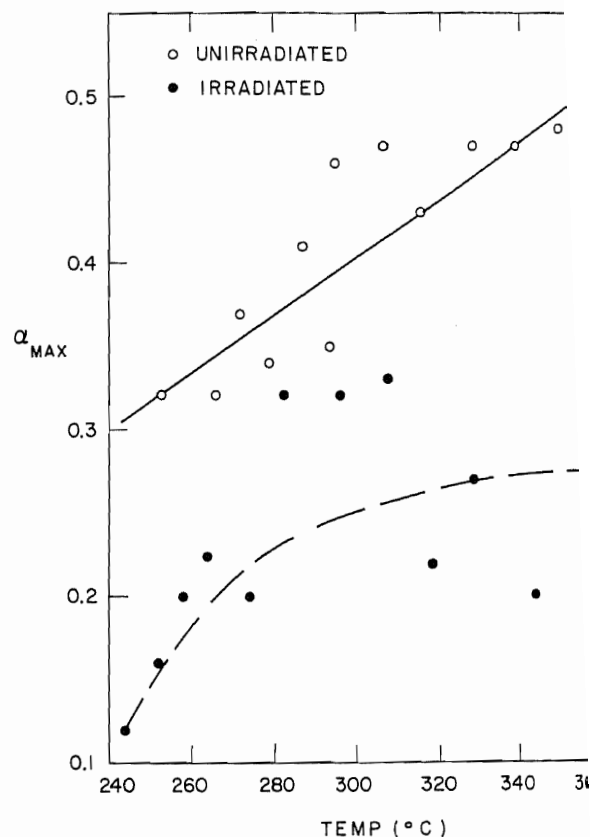


Figure 5. α_{\max} *vs.* temperature.

an increase of temperature causes an increase in α_{\max} , the scatter is too large to allow a definite conclusion.

Discussion

We believe that the results can be interpreted in terms of the following topochemical model. Reaction begins at the surface of each crystallite from a certain number of potential nuclei which become activated by thermal fluctuations. Growth then proceeds two-dimensionally into the crystallite, probably along preferred planes. The square law is evidence for this. Jacobs and Kureishy⁴ draw the same conclusion. The activation energy for the nucleation process is somewhat lower than that for growth. Irradiation enhances the number of potential nuclei but does not affect the rate of growth.

The justification for this model is as follows. The complexity in the Arrhenius plot indicates that two or more processes of different activation energies are occurring simultaneously. There are many reasons for believing that these two processes are nucleation and growth. At the beginning of the reaction these two processes would occur simultaneously and the activation energy (k_L) would represent some complex

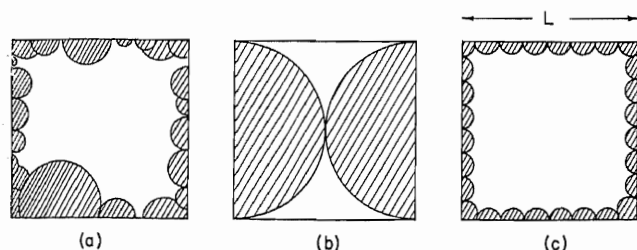


Figure 6. Simplified topochemical model.

posite of that for nucleation and growth and would be higher than for growth alone. At the end of the reaction where nucleation is either complete or its effects completely dominated by growth, the activation energy (k_a) is much lower and represents growth alone.¹⁰ If the activation energy for growth is higher than for nucleation, it is expected that at elevated temperatures growth would dominate the rate ($d\alpha/dt$). This is responsible for the diminishing value of the slope in the Arrhenius plot at high temperatures. The fact that the value of the power " m " settles down to a value of 2 (even for no α_0 correction) at high temperatures tends to confirm the hypothesis that growth alone is dominant in causing a given amount of decomposition, for the nucleation, which is shown below to add one to the power m , is not effective, whereas at low temperatures the power is higher than 2 (see Appendix). It is of interest to note that Jacobs and Kureishy obtain a value of $m = 2$. The model is further strengthened by the behavior of α_{\max} . This quantity represents that stage of the reaction when growing nuclei begin to overlap. A simplified picture of this process is shown in Figure 6a where random nucleation (in terms of position and time) began on the surface and pictures the situation at the maximum rate or α_{\max} . Clearly any further reaction results in a contracting area and thus smaller values of $d\alpha/dt$. The fact that α_{\max} is higher at higher temperatures means that less nuclei can be formed before the maximum rate stage. An extreme case is shown in Fig. 6b where only two nuclei could be formed before the rapidly growing nuclei overlapped. In this case $\alpha_{\max} = 79\%$ as compared to 21% for the situation represented by Fig. 6c.

The effects of irradiation tend to confirm the correctness of the model. The induction period is vastly reduced as would be the case if the number of potential nuclei were increased by the irradiation, for then the time required to reach any given rate must be reduced. There are two concurrent events at the beginning of the reaction, nucleation and growth. Since there are now so many more potential nuclei and hence more growing nuclei after a given time, the power law tends

to reflect growth alone and so the observed drop in " m " to 2 upon irradiation, even without any α_0 correction, is understandable. The drop in activation energy of the beginning stages of reaction upon irradiation is also understandable, since now the activation energy is closer to that for pure growth. The maximum rate is unaffected by irradiation. Referring to Fig. 6c one can make a simplified calculation of the maximum rate as follows: Suppose there are N nuclei and L is the length of the side of the crystallite (assumed to be a square). The radius of each nucleus (assuming they all started growing at the same time and were equally spaced around the crystallite) is $2L/N$. If the reaction front moves with a velocity ν , it can be easily shown that

$$\left(\frac{d\alpha}{dt}\right)_{\max} = \frac{2\pi\nu}{L} \quad (5)$$

which is independent of N .¹¹ This equation also shows why the activation energy for the maximum rate is unaffected by irradiation, since the only temperature dependent quantity in eq. 5 is ν which we believe is not affected by irradiation. However, the fact that N is larger with irradiated material implies that the value α_{\max} would be lower. Figure 5 shows that indeed this is the case. It is also easy now to understand why the activation energy is changed by irradiation only near the beginning of the reaction for in the later stages the growth of existing nuclei masks growth due to new nuclei since the former are so much bigger.

There remains the decay stage. The fact that it follows a simple exponential decay rather than a contracting area formula does not mean that a contracting area mechanism is not operative. This has been amply demonstrated in the literature.¹²

There are many complicated events that can render the decay stage exponential. An exponential particle size distribution resulting from break-up due to strains is one example. We, therefore, have no reason to believe that the decay stage is anything other than a continuation of the growth after nuclei overlap. One would then, of course, not expect irradiation to have any effect since nucleation has at this point long

(10) The amount of decomposition contributed by a nucleus of radius r growing two-dimensionally is proportional to r^2 . A nucleus of any size other than the very smallest and newest will contribute very much more to the total decomposition than will a newly born growth nucleus.

(11) At the maximum rate, the radius of each nucleus is $2L/N$ and the total length of the reaction "front" is $2\pi L(N-2)/N$. In time dt , the increase in area $da = 2\pi L(N-2)\nu dt/N$ and therefore the increase in α , $d\alpha = da/L^2 = 2\pi(N-2)\nu dt/NL$. Therefore, $(d\alpha/dt)_{\max} = 2\pi(N-2)\nu/NL$; when N is large, $(d\alpha/dt)_{\max} = 2\pi\nu/L$.

(12) See, for example, J. Jach, ref. 4, p. 8.

ceased to be influential. This lack of effect is demonstrated in Fig. 4.

Acknowledgment. The authors wish to thank Miss E. Moorehead for her help in the experimentation and curve fitting.

Appendix

The supposed nucleation results from random thermal fluctuations. Their number will then be given as a function of time t by

$$N_0[1 - \exp(-kt)]$$

where N_0 is the number of potential nuclei, k being a rate constant. If the velocity of radial growth of a nucleus is ν and L^2 is the area of a platelet then

$$\alpha = \frac{kN_0\pi\nu^2}{2L^2} \int_0^t (t-y)^2 e^{ky} dy$$

where the integration accounts for nuclei beginning to grow at time $t = y$.¹³

This equation evaluates to

$$\alpha = \frac{N_0\pi\nu^2}{k^2L^2} \left[1 - kt + \frac{k^2t^2}{2} - \exp(-kt) \right]$$

This equation reduces to a t^3 dependence for small t and t^2 for high t , at which point the effect of nucleation is outweighed by the t^2 growth dependence.

(13) For more details, see W. E. Garner, "Chemistry of the Solid State," Butterworths Inc., Washington, D. C., 1955, Chapter 1.